

Resonance energy transfer from a fluorescent dye molecule to plasmon and electron-hole excitations of a metal nanoparticle

R. S. Swathi and K. L. Sebastian

Department of Inorganic and Physical Chemistry

Indian Institute of Science, Bangalore 560012, India

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We study the distance dependence of the rate of electronic excitation energy transfer from a dye molecule to a metal nanoparticle. Using the spherical jellium model, we evaluate the rates corresponding to the excitation of $l = 1, 2$, and 3 modes of the nanoparticle. Our calculation takes into account both the electron-hole pair and the plasmon excitations of the nanoparticle. The rate follows conventional R^{-6} dependence at large distances while small deviations from this behavior are observed at shorter distances. Within the framework of the jellium model, it is not possible to attribute the experimentally observed d^{-4} dependence of the rate to energy transfer to plasmons or e-h pair excitations.

I. INTRODUCTION

Fluorescence Resonance Energy Transfer (FRET) is an interesting photo-physical process [1] that involves transfer of excitation energy from donor to acceptor in a non-radiative fashion. It has been extensively used in biology as a spectroscopic ruler to study the conformational dynamics of biopolymers in the 10-100 Å range. The rate of non-radiative damping of dye molecules near quencher molecules is found to vary as R^{-6} , where R is the distance between the donor and the acceptor. In FRET, energy is transferred from a donor molecule to an acceptor molecule via the dipole-dipole interaction. The matrix element for the interaction is given by $V_{DA} \propto \frac{|\bar{\mu}_D||\bar{\mu}_A|}{R^3}$ where $\bar{\mu}_D$ and $\bar{\mu}_A$ are the transition dipole moments of donor and acceptor. Therefore, the rate of energy transfer, which is proportional to the square of the interaction matrix element varies as R^{-6} . The Förster expression for the rate is given by $k_{nr} = k_r \left(\frac{R_0}{R} \right)^6$ where k_r is the radiative rate and R_0 is the Förster radius, which can be expressed as an overlap integral between the donor emission and acceptor absorp-

tion spectra as $R_0 \propto \left(\kappa^2 \int \frac{d\omega}{\omega^4} I_D(\omega) \alpha_A(\omega) \right)^{\frac{1}{6}}$. The orientation factor κ^2 takes into account the effect of relative orientation of the donor and acceptor transition dipole moments and is given by $\kappa^2 = (\sin \theta_A \sin \theta_D \cos(\varphi_A - \varphi_D) - 2 \cos \theta_A \cos \theta_D)^2$. The value of κ^2 is usually taken to be $\frac{2}{3}$ assuming rapid orientational averaging of the donor within the lifetime of its excited state [2].

However, there are reports of deviations from the conventional FRET behaviour in the literature. Two possible reasons for this are the breakdown of point dipole approximation, especially for systems with extended transition densities like polymers [3] and the incomplete orientational averaging within the lifetime of the excited state [4]. Currently, there is a lot of interest in using nanoparticles [5] as quenching agents due to their tunable optical properties [6]. There have been very interesting observations on energy transfer between the dye fluorescein and a gold nanoparticle of diameter 1.4 nm . Using double stranded DNA as the spacer, the dye molecule was kept at different fixed distances from the particle and the rate of energy transfer was experimentally determined [7, 8]. They found a d^{-4} dependence of the rate on the distance d between the dye and the surface of the nanoparticle and have referred to this as nanoparticle surface energy transfer (NSET). Such a dependence is of great interest as it would more than double the range of distances that can be measured. Persson and Lang (PL) [9] had long ago studied the dissipation of vibrational energy of an oscillating dipole held at a distance d above the surface of a semi-infinite metal. In this case, the energy is transferred to electron-hole (e-h) pair excitations in the metal, which form a continuum, having all possible energies from zero to infinity. For an excitation energy ω , their density of states is proportional to ω . PL found the distance dependence to be $\sim d^{-4}$ (see also [10, 11]). Following this, it is suggested [7, 8] that the observed distance dependence in NSET is due to the excitation of e-h pairs in the nanoparticle. In support of this, the authors [7, 8] point out that plasmonic absorptions have not been observed for a gold nanoparticle of diameter 1.4 nm . However, unlike a semi-infinite metal, a nanoparticle of such a small size, does not have a continuum of e-h excitations. The excitations are discrete (see the excitation spectrum given in Fig. 2 of this paper). In view of this, it would be very interesting to study the distance dependence of NSET theoretically.

There have been attempts to explain the d^{-4} dependence for the case of nanoparticle [12, 13, 14]. In particular, focus of these papers [14] is on energy transfer to the plasmons of

the nanoparticle and they find a predominantly R^{-6} dependence, though deviations occur at shorter distances. These calculations do not account for e-h pair excitations. To the best of our knowledge, there are no reports of theoretical calculations which take plasmons as well as e-h excitations of the nanoparticle into account. Therefore, we have calculated the rate of transfer of electronic excitation from an excited fluorescein molecule to a 1.4 nm nanoparticle, taking both the e-h pair excitations as well as the plasmon excitations of the nanoparticle into account. We model the nanoparticle within the jellium model [15], and use time dependent local density approximation (TDLDA) to calculate the excitations of the nanoparticle. Strictly speaking, one should use RPA with the Hartree Fock approach as the starting point, because in any LDA based approach, the single particle energies and the response calculated using them have no fundamental meaning. However, there have been a number of calculations based on TDLDA for the response of a metallic nanoparticle and other systems [16, 17, 18, 19]. All these calculations have led to results which agree well with experiments and therefore we use this approach. Within this framework, we do not get the experimentally observed d^{-4} dependence. Therefore, in our opinion, this very interesting experimental observation is, as it stands, unexplained. Perhaps, it may be due to other factors, like transfer through the DNA, or the asphericity of the nanoparticle, which are being currently investigated. It is also to be noted that the distances between the donor and the acceptor in the NSET experiment are much greater than the dimensions of the donor and acceptor, making it unlikely that the breakdown of point dipole approximation is responsible for the d^{-4} dependence.

II. MODEL FOR THE NANOPARTICLE

We use the spherical jellium model for the nanoparticle which provides a model system for investigating the response of the conduction electrons in small metal particles [20, 21]. In this model, the positive ions of the metal cluster are replaced by a uniform sphere of positive charge and the density functional formalism within the linear response approximation is used to calculate the response of the cluster to the time dependent external potential. Two kinds of excitations are possible for a metal cluster namely, single particle excitations and plasmon excitations. In a single particle excitation, an electron is excited from an occupied level to an unoccupied level and these are the electron-hole pair excitations. Plasmon excitations

are collective oscillations involving many electrons, wherein the electronic charge density oscillates as a whole against the positive background.

We denote the Hamiltonian of the nanoparticle as H_0 . The molecule is treated within a single particle model. An electron which was initially in the orbital ϕ_g is excited to an orbital ϕ_e . De-excitation of the molecule, in which the electron goes back to ϕ_g may be thought of as a time dependent potential acting on the nanoparticle, given by

$$\Phi_{ext}(\bar{r}, t) = e^{-i\omega t} \int \frac{\phi_e^*(\bar{r}') \phi_g(\bar{r}')}{|\bar{r} - \bar{r}'|} d\bar{r}'. \quad (1)$$

In the above, ω is the frequency of the transition corresponding to de-excitation. Thus the total Hamiltonian can be written as:

$$H = H_0 + \Phi_{ext}(\bar{r}, t). \quad (2)$$

One can carry out an expansion of the electrostatic potential at \bar{r} due to a charge distribution at \bar{r}' as [22]

$$\frac{1}{|\bar{r} - \bar{r}'|} = \sum_{l,m} \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{l,m}^*(\Omega) Y_{l,m}(\Omega'), \quad (3)$$

where $r_>$ ($r_<$) is the larger (smaller) of r and r' and $Y_{l,m}(\Omega)$ are the spherical harmonics. From Fig. 1, it is obvious that the integration over \bar{r}' is to be performed over the molecule. As the electron density of the molecule is fully outside the nanoparticle, $r < r'$ and hence

$$\Phi_{ext}(\bar{r}, t) = e^{-i\omega t} \sum_{l,m} M_{l,m} r^l Y_{l,m}^*(\Omega) \quad (4)$$

where

$$M_{l,m} = \frac{4\pi}{2l+1} \int \frac{\phi_e^*(\bar{r}') \phi_g(\bar{r}')}{r'^{l+1}} Y_{l,m}(\Omega') d\bar{r}'. \quad (5)$$

Thus the perturbation acting on the nanoparticle is a combination of multipole fields of the form $r^l Y_{l,m}^*(\Omega)$ for various values of l and m . The case of such perturbations acting on nanospheres of jellium is well studied in the literature [23].

III. THE RATE OF ENERGY TRANSFER

The rate of transfer using the Fermi golden rule is:

$$k = \frac{2\pi}{\hbar} \sum_E |\langle E | \Phi_{ext}(\bar{r}, t) | G \rangle|^2 \delta(E_E - E_G - \hbar\omega) \quad (6)$$

where $|G\rangle$ is the initial (ground) and $|E\rangle$ is the final (excited) state of the nanoparticle. For a spherically symmetric closed-shell system [24], within the jellium model, the perturbation $r^l Y_{l,m}^*(\Omega)$ can only lead to the excitation of the lm^{th} mode in the nanoparticle. Thus, the excitations in the nanoparticle have the same symmetry as the perturbation and the rate simplifies to

$$k = \frac{2\pi}{\hbar} \sum_{E,lm} M_{l,m}^2 |\langle E_{l,m} | r^l Y_{l,m}^*(\Omega) | G \rangle|^2 \delta(E_{E_{l,m}} - E_G - \hbar\omega). \quad (7)$$

$|E_{l,m}\rangle$ denotes excited states having quantum numbers l, m .

If the nanoparticle is placed in an oscillatory external field $\Phi_{ext}^l(r)e^{-i\omega t} = r^l e^{-i\omega t}$, an induced electronic charge density is set up, which within the linear response theory [17, 21] is given by

$$\delta\rho_l(r) = \int dr' \Pi_l(r, r', \omega) \Phi_{ext}^l(r') \quad (8)$$

where $\Pi_l(r, r', \omega)$ is the density-density correlation function or the polarization propagator. Within the random phase approximation (RPA), $\Pi_l(r, r', \omega)$ obeys the following integral equation: [17, 21]

$$\Pi_l(r, r', \omega) = \Pi_l^0(r, r', \omega) + \int dr_1 \int dr_2 \Pi_l^0(r, r_1, \omega) \kappa_l(r_1, r_2) \Pi_l(r_2, r', \omega) \quad (9)$$

where $\Pi_l^0(r, r', \omega)$ is the independent particle propagator and $\kappa_l(r_1, r_2)$ is the effective two particle interaction [21]. The independent particle approximation to the response function $\Pi_l^0(r, r', \omega)$, contains the e-h pair excitations only, while the response under RPA, given by $\Pi_l(r, r', \omega)$ includes both the single particle and plasmonic response. The free and RPA response to the external perturbation of the system is calculated by integrating the external potential over the transition density[17, 21]. Thus we have

$$\Pi_l^0(\Phi_{ext}^l, \omega) = \int dr \Phi_{ext}^l(r) \delta\rho_l^0(r) \quad (10)$$

and

$$\Pi_l^{RPA}(\Phi_{ext}^l, \omega) = \int dr \Phi_{ext}^l(r) \delta\rho_l^{RPA}(r) \quad (11)$$

The polarization propagator is related to the strength function, $S_l(\omega)$ by

$$S_l(\omega) = \frac{1}{\pi} \text{Im} \Pi_l(\Phi_{ext}^l, \omega). \quad (12)$$

The rate may be expressed in terms of the strength function $S_l(\omega)$ as

$$k = \frac{2\pi}{\hbar} \sum_{E,lm} M_{l,m}^2 S_l(\omega) \quad (13)$$

The evaluation of polarization propagator for the independent particle as well as the RPA response allows one to take both the e-h pair excitations as well as the plasmonic excitations into account in the calculation. We make use of the time dependent local density approximation (TDLDA) version of the above equations, as this has been found to lead to excellent results. Details of the approach may be found in [17, 21].

IV. CALCULATIONS

We have optimized the geometry of fluorescein, using the Gaussian03 program, within the DFT approximation (B3LYP-6-31G*). The HOMO (ϕ_g) and LUMO (ϕ_e) were taken from the calculation for the optimised geometry. These orbitals were then used to evaluate the matrix elements $M_{l,m}$ numerically for all m with l up to 3. A grid within a box of size $24\text{\AA} \times 24\text{\AA} \times 24\text{\AA}$, within which the molecule was located was used for this purpose. Note that $l = 1$ corresponds to the oscillation of the electrons in the nanoparticle that has the shape of a p-orbital, $l = 2$ that of a d-orbital and $l = 3$ that of an f-orbital. We assumed an Au cluster of 90 atoms which corresponds to a 1.4 nm gold nanoparticle and performed the jellium model calculation to evaluate $\Pi_l^0(\Phi_{ext}^l, \omega)$ and $\Pi_l^{RPA}(\Phi_{ext}^l, \omega)$. The rate was calculated using Eq. (13), with static but random averaging over all the orientations of the nanoparticle. Thus, we have evaluated the rate of energy transfer from the fluorescein molecule to the 1.4 nm gold nanoparticle as a function of distance.

V. RESULTS AND DISCUSSION

The rate of energy transfer depends on the values of the two terms $M_{l,m}$ and $S_l(\omega)$. The first one represents the perturbing potential acting on the nanoparticle due to the dye molecule and the second one is the response of the nanoparticle to the perturbation. We have evaluated $S_l(\omega)$ for $l = 1, 2$ and 3 modes of excitations of the nanoparticle, for the TDLDA response using the JELLYRPA program of Bertsch [21]. For the calculation, we have taken $r_s = 3$ atomic units (au). The broadening parameter Γ , which determines the width of the single particle peaks was taken to be 0.01 eV . Plot of $S_l(\omega)$ calculated using the single particle and RPA approaches is shown in Fig. 2 for $l = 1, 2$ and 3 modes. The TDLDA plot clearly shows peaks corresponding to e-h pair excitations, collective surface plasmon

l	$S_l(\omega)$ (SP) ($a.u.^{2l}/eV$)	$S_l(\omega)$ (TDLDA) ($a.u.^{2l}/eV$)
1	32.69	14.32
2	259500.	322.4
3	5.714×10^6	3.988×10^6

TABLE I: Numerical values of $S_l(\omega)$ for $l = 1, 2$ and 3 at $\omega = 2.4eV$, the emission energy for fluorescein. SP stands for single particle.

and bulk plasmon excitations. The numerous narrow spikes at lower energies correspond to e-h pair excitations. The peak around $\omega/\omega_B \simeq 0.5$ is the remnant of the surface plasmon and the one around $\omega/\omega_B \simeq 1.2$ corresponds to the bulk plasmon. Note that the frequency of a surface plasmon mode [25] is related to that of the bulk plasmon mode as $\omega_S = \omega_B \sqrt{\frac{l}{2l+1}}$. The surface plasmon mode is slightly red shifted while the bulk plasmon mode is slightly blue shifted. The shifts are consistent with previous jellium model calculations [20, 23]. The quantities of interest to us, in the calculation of the rate of energy transfer to the nanoparticle are $S_l(\omega)$ for $l = 1, 2$ and 3 , with ω having the value of emission energy of the dye particle, which are given in Table 1 for $\omega = 2.4eV$.

After evaluating $M_{l,m}$ numerically for all m with l upto 3, we evaluated the rates of transfer corresponding to the $l = 1, 2$ and 3 modes of excitation of the nanoparticle, both for the single particle as well as the TDLDA response. The results for TDLDA are shown in Fig. 3. Note that the expansion in Eq. (3) and hence the calculations are not valid if the dye penetrates into the electron density of the nanoparticle. Moreover, in such a case, overlap effects dominate and one has to think of the Dexter mechanism and evaluate the exchange integral. The rates for $l = 1, 2$ and 3 modes vary with distance as R^{-6} , R^{-8} and R^{-10} as may be seen from the slopes in Fig. 3. Then, we evaluated the total rate of transfer, again for single particle as well as TDLDA response (see Fig. 4). It is found from the figure that the single particle rate is actually larger than the TDLDA result. This is because there is intensity borrowing by the collective modes (bulk and surface plasmons) from the single particle excitations, resulting in a lower value for $S_l(\omega)$ in the TDLDA calculations, as is clear from table I. Asymptotically, at large distances, it is only the $l = 1$ mode that is

important and this leads to the conventional $\sim R^{-6}$ limit for the total rate. But, at shorter distances, $l = 2$ and 3 modes gain importance leading to deviations from R^{-6} behavior at shorter distances. To make this clearer, we fitted the long distance rate with $\frac{c}{R^6}$ and used the result to calculate the short distance rate. The resultant rate is shown in Fig. 4, along with the actual rate. The actual rates are found to be *slightly higher* than expected from $\sim R^{-6}$ dependence. This is due to the fact that $l = 2$ and 3 modes become important at lower distances. *Note that the deviations are not such as to give an R^{-4} dependence in the distance range that we study.* It is also of interest to note that the R dependence is governed by $|M_{l,m}|^2$ and not by $S_l(\omega)$. Use of a different set of values of r_s , or ω would not change the R dependence. Therefore, we conclude that excitation of plasmons or e-h pairs cannot lead to the observed experimental data. In ref. [14], for a distance range from infinity to up to 4 times the radius of the nanoparticle (for our case, 28 \AA), the behavior is found to be R^{-6} . In this range, we too get an R^{-6} dependence, illustrating that inclusion of e-h pair excitations does not affect the result at all. Also, it is to be noted that in our calculations, our grid used for numerical integration will penetrate into the nanoparticle for distances less than about 28 \AA so that our approach will break down for closer distances.

VI. CONCLUSIONS

We have adopted a spherical jellium model to evaluate both the independent particle and collective response of a metallic nanoparticle to an external time dependent perturbation and used this to evaluate the rates of non-radiative energy transfer from the excited state of a fluorescent dye to the particle. The rates due to the excitation of $l = 1, 2$ and 3 modes of the nanoparticle were found to vary with distances as R^{-6} , R^{-8} and R^{-10} respectively. The major contribution to the rate is from the leading R^{-6} term. The contributions from the other terms are relatively small, except at distances close to 28\AA , and these make the rate only larger and they are not in a direction as to make the result behave like d^{-4} . Thus the experimentally observed d^{-4} dependence cannot be explained by considering the excitation of plasmons or e-h pairs of the nanoparticle.

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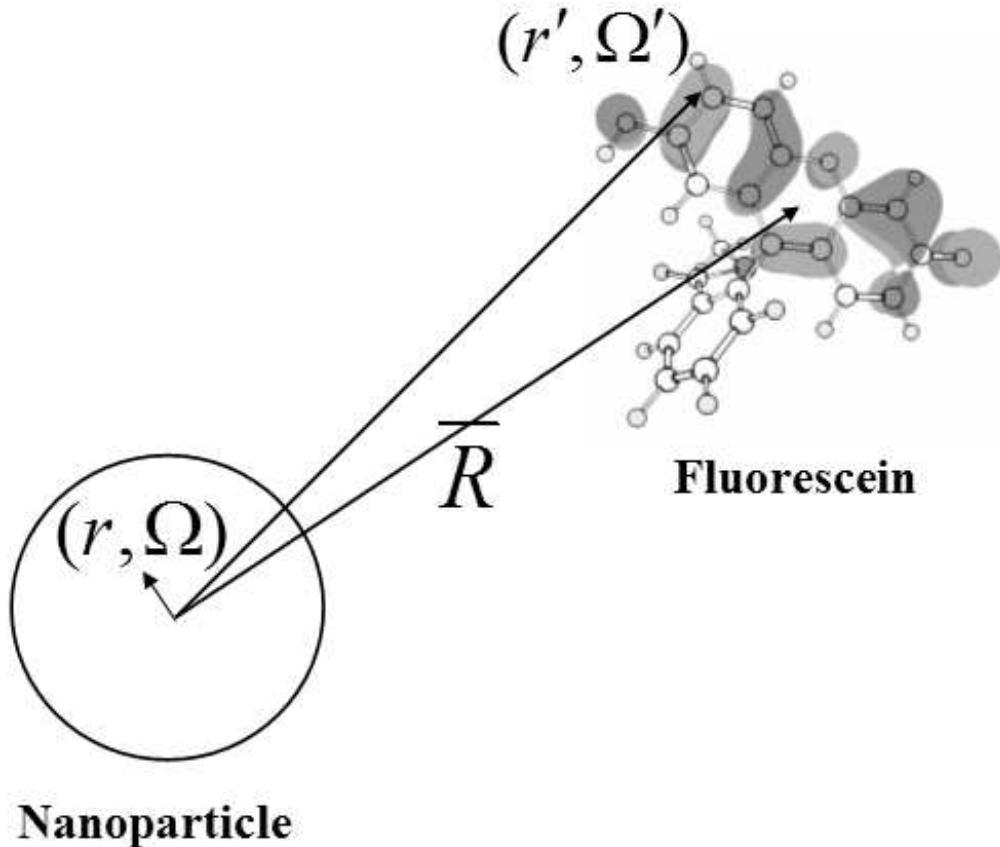


FIG. 1: A schematic of the system consisting of the gold nanoparticle and the dye molecule.

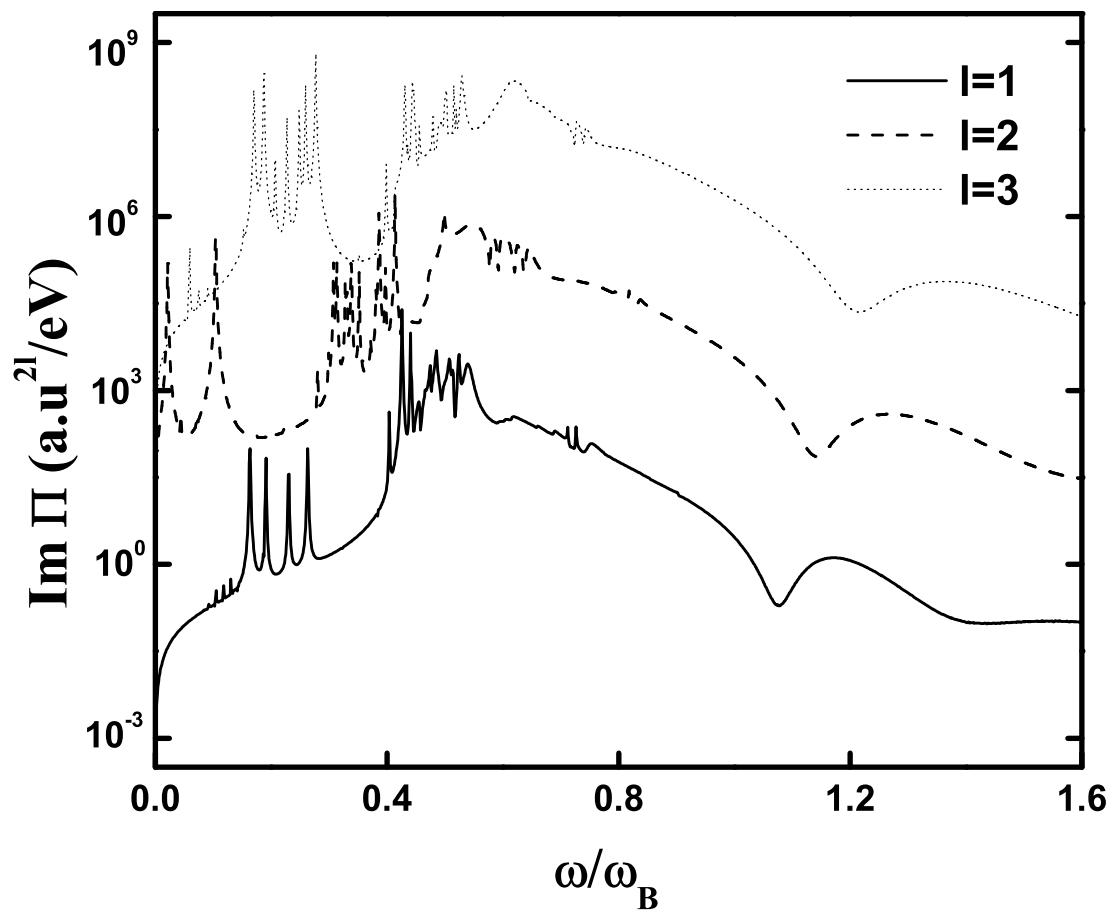


FIG. 2: The imaginary part of the RPA polarization propagator for the excitation of $l = 1, 2$ and 3 modes of the nanoparticle. The frequency is given in units of the bulk plasmon frequency.

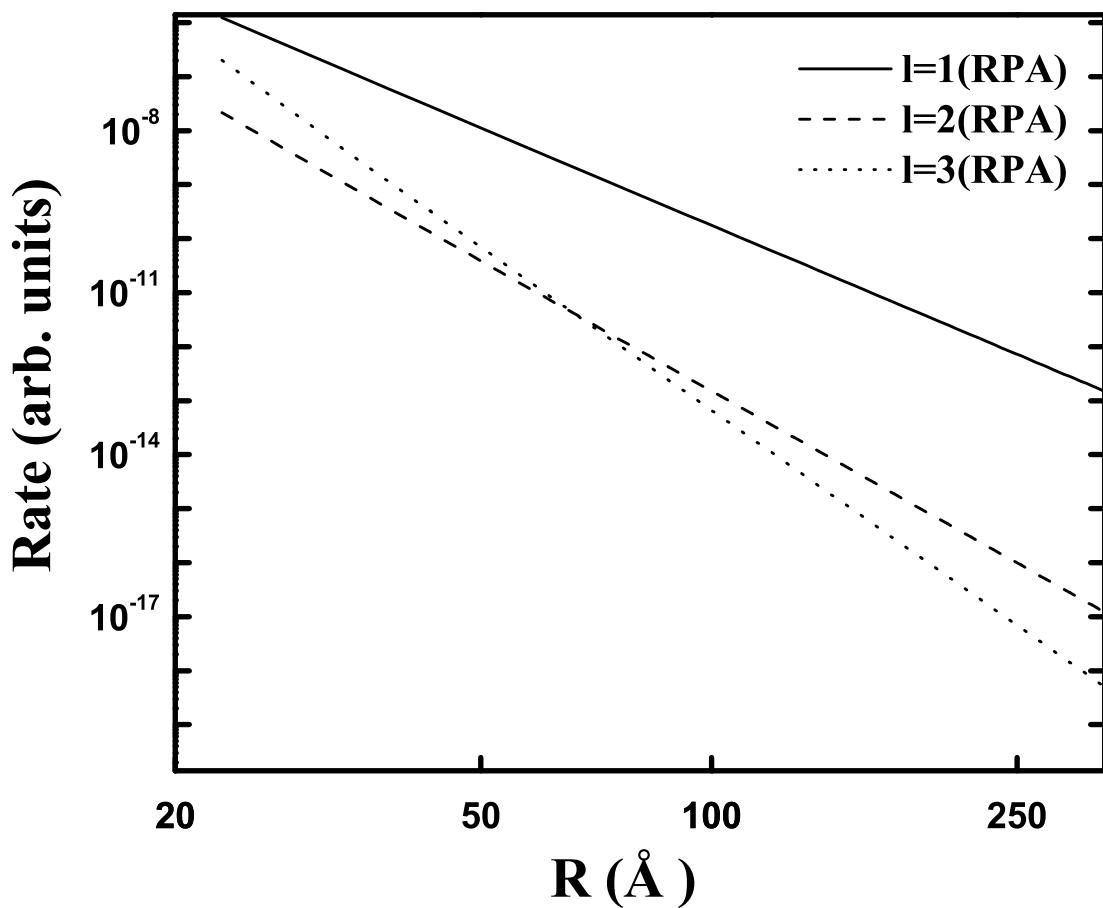


FIG. 3: Distance dependence of the rate of transfer corresponding to the excitation of $l = 1, 2$ and 3 modes of the nanoparticle for the TDLDA response. The slopes of the log-log plots are -6.005 , -8.019 and -10.039 for $l = 1, 2$ and 3 respectively.

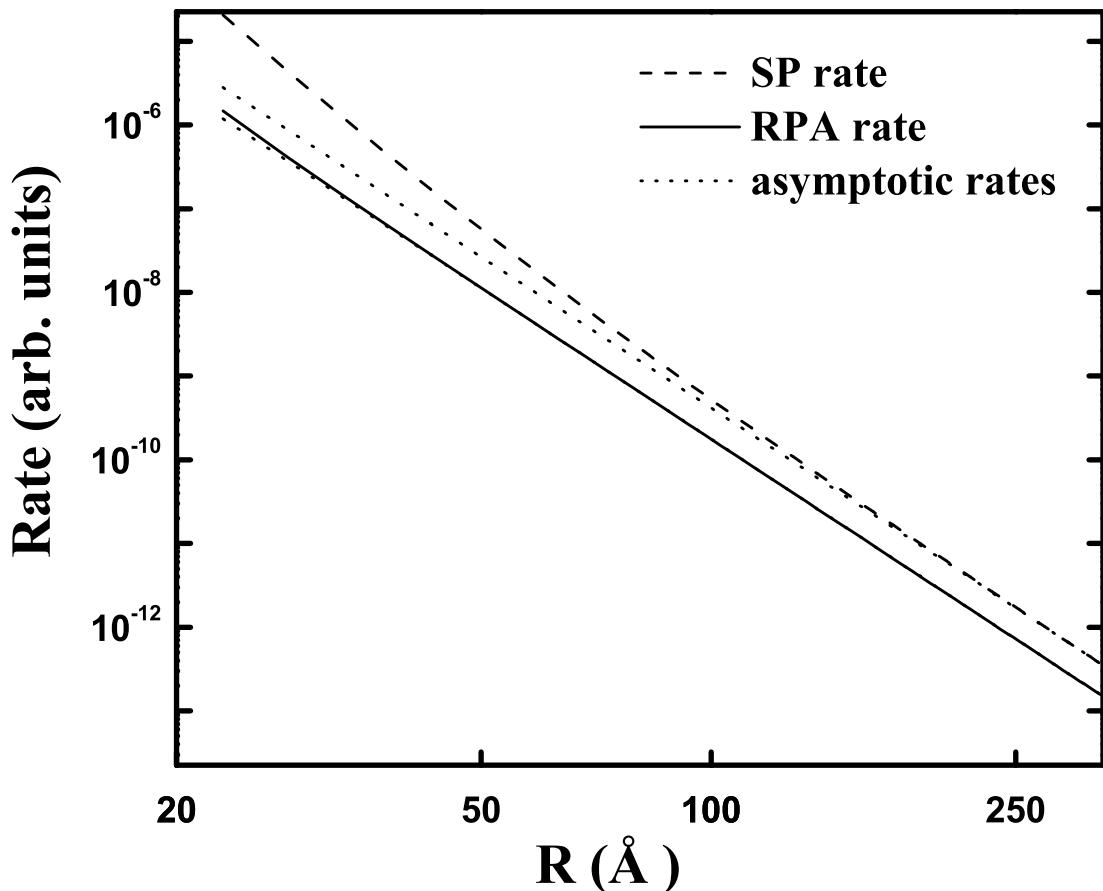


FIG. 4: Distance dependence of the calculated total rate of transfer for the single particle and RPA responses. In both the cases, the rate calculated using asymptotic expression c/R^6 (referred to as asymptotic rates) are shown as dotted lines. The actual rate is greater than this due to the contributions from $l = 2$ and $l = 3$ modes.